III.A.13 Highly Textured Glass Composite Seals for Intermediate-Temperature SOFCs

Objectives

- Fabricate a compliant seal that is hermatic at solid oxide fuel cell (SOFC) operating conditions.
- Achieve target leak rates with minimum compressive loading.
- Identify a glass composition that is chemically compatible with a metal interconnect and does not support chromium migration or silicon degradation.

Accomplishments

- Identified powder characteristics for glass and zirconia powders to formulate dense and low shrinkage composite at 850°C.
- Fabricated glass-ceramic composite seal that demonstrates a leak rate below 0.094 sccm/cm with seal area pressurized to 13.8 kPa with helium. Seal was measured from 650-850°C at 0.55 MPa compressive load.
- Demonstrated stable seal performance for over 50 hours with multiple pressurization cycles.

Introduction

Many planar SOFC designs have been proposed using a number of sealing materials, with mixed degrees of success. The simplest methods have been single composition glass seals, which have been compositionally designed to melt at relatively low temperature and yet maintain sufficient viscosity at the operating temperature to provide a robust seal [1,2]. More complex approaches have attempted to use multiple glass phases in layers or to add a minority fraction of ceramic particles to the mixture to fulfill the seal requirements [3,4].

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These experiments focus on the development of a composite sealing system for intermediate-temperature solid oxide fuel cells (600-800°C). These two-phase glass/ceramic mixture structures are targeted to provide high durability, low cost and scalability for manufacturing. The proposed seals combine a crystalline ceramic phase that will provide a skeletal structure to the seal, and a glass matrix that will improve wetting at the seal interfaces and allow the seal to densify at lower operating temperatures. The composite structure is also anticipated to provide a degree of compliance to the stack at the operation temperature.

Approach

Two approaches have been evaluated–the development of isotropic seal materials, in which equiaxed ceramic powders have been added to a glass matrix, and the development of textured seal materials, in which anisotropic ceramic particles have been oriented in a glass matrix. Examples of the resultant structures are shown in Figures 1 and 2. In both cases, it is expected that the majority crystalline phase will dominate the thermal expansion behavior and present a tortuous path for gas species with the possible added benefit of the textured seals in improved fracture toughness and creep resistance.

A range of particulate materials and glass compositions have been evaluated to determine those best suited for SOFC sealing applications. This paper documents the development of isotropic seal materials and their validation testing.

Results

Figure 1 shows the results of the sintering study for the composite mixtures of the selected seal material and zirconia powder at 850°C. The surface area of the seal material and zirconia powder was 4 m^2/g and 1.5 m^2/g, respectively. The two powders were mixed in varying ratios by ball milling mixtures of the glass and zirconia powder. The study showed that the composites with seal material content of less than 50% saw little

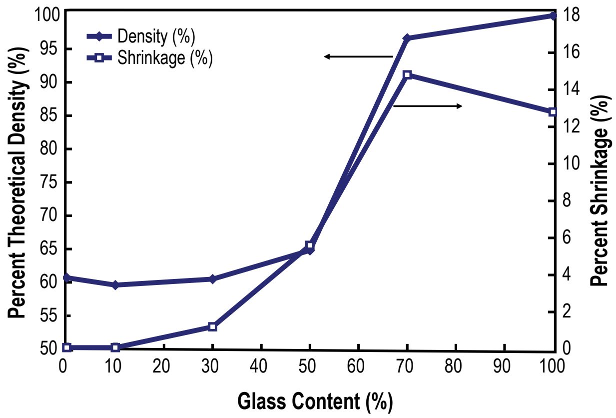

FIGURE 1. Impact of Glass Content on Composite Densification and Shrinkage

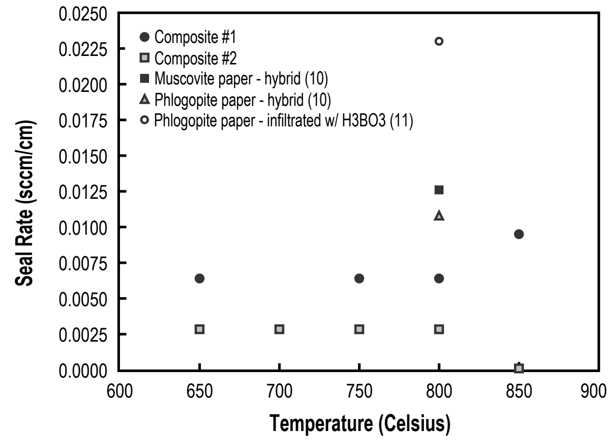

FIGURE 2. Screening Tests

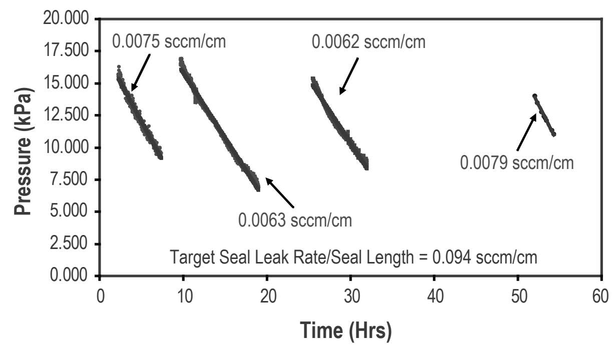

FIGURE 3. Long Term Seal Test

to no improvement in density over the pure zirconia samples. The composites with seal material content greater than 70% achieved over 95% density with shrinkage over 14%. The pure glass material sample achieved 100% density at 850°C with approximately 13% shrinkage. Based on this assessment, for this mixture of powders, a high glass content was selected. Alternative formulations (particularly those using higher surface area glasses) use higher concentrations of the crystalline component.

Figures 2 and 3 provide composite seal performance data obtained using the 70% glass formulations identified in Figure 1. In Figure 2, a screening test of short term performance, the calculated leak rate for two composites utilizing similar compositions to that described in Figure 1 but with varying glass formulations is compared. Both seals perform well below the targeted leak rate of 0.094 sccm/cm at all temperatures and below reported values for seals tested under similar conditions [5,6].

The seal test target leak rate was calculated based upon the metric of 1% fuel loss. A fuel flow rate of 376 sccm was calculated based upon a fuel cell with the following specifications: area of 81 cm^2, current density of 0.5 A/cm^2, and 75% fuel utilization. The amount of fuel loss was then determined to be 3.76 sccm. The seal length (40 cm) is the perimeter of a 10 cm square seal. Finally, the target seal leak rate of 0.094 sccm/cm is obtained by dividing the fuel loss by the seal length.

Figure 3 shows pressure decay curves for a promising seal material, demonstrating stable seal performance over 50 hours with multiple pressurization cycles. The pressure decay data has been analyzed to determine the leak rate over several hours, before the pressure was again raised to the starting value on a periodic basis. Based on the pressure decay data, it is clear that the seals retain their hermeticity over the 50-hour test. Ongoing evaluations are being performed to determine the applicability of the reported seals during fuel cell operation.

Conclusions and Future Directions

Using a combination of glass formulations and crystalline materials, a range of seal materials have been developed. Using *in situ* measurements of seal performance, materials offering good hermeticity have been identified. Continuing evaluations of performance under fuel cell operation are underway.

Special Recognitions & Awards/Patents Issued

1. Best Commercial Presentation, "Composite Seals for Intermediate Temperature SOFCs," ASM International Conference on Joining of Advance and Specialty Materials VII, October 18-20, 2004, Columbus, OH.

FY 2006 Publications/Presentations

1. "Composite Seal Development and Evaluation." Presentation at 30st International Conference and Exposition on Advanced Ceramics and Composites, January 22-27, 2006, Cocoa Beach, FL.

2. "Composite Seal Development and Evaluation." Manuscript for Proceeding of 30st International Conference and Exposition on Advanced Ceramics and Composites, January 22-27, 2006, Cocoa Beach, FL.

References

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2. I.D. Bloom and K.L. Ley, U.S. Patent No. 5,453,331.

3. Y. Harufuji, Japanese Patent JP04-47,672.

4. L.A. Xue, US Patent No. 6,271,158.

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6. Y.S. Chou et al., J. of Power Sources 135 (2004) 72-78.